

CASE PP/1-22228/A

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE APPLICATION OF

Group Art Unit: 1714

DAVID GEORGE LEPPARD ET AL

Examiner: K. A. Sanders

APPLICATION NO: 09/912,139

Confirmation No. 4093

FILED: JULY 24, 2001

FOR: TRANSPARENT POLYMER ARTICLES OF
LOW THICKNESS

Commissioner for Patents

P.O. Box 1450

Alexandria, VA 22313-1450

CLAIM OF PRIORITY UNDER 35 USC 119

Sir:

Applicants in the above-entitled application by their agent hereby claim priority under the International Convention of Europe (designating Germany) application No. 00810666.8, filed on July 26, 2000. This application is acknowledged in the Declaration of the instant case.

A certified copy of said European application is submitted herewith.

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Bescheinigung

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Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

00810666.8

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

I.L.C. HATTEN-HECKMAN

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Blatt 2 der Bescheinigung
Sheet 2 of the certificate
Page 2 de l'attestation

Anmeldung Nr.:
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Anmelder:
Applicant(s):
Demandeur(s):
Ciba Specialty Chemicals Holding Inc.
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SWITZERLAND

Bezeichnung der Erfindung:
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Titre de l'invention:
Transparent polyolefin articles of low thickness

In Anspruch genommene Priorität(en) / Priority(ies) claimed / Priorité(s) revendiquée(s)

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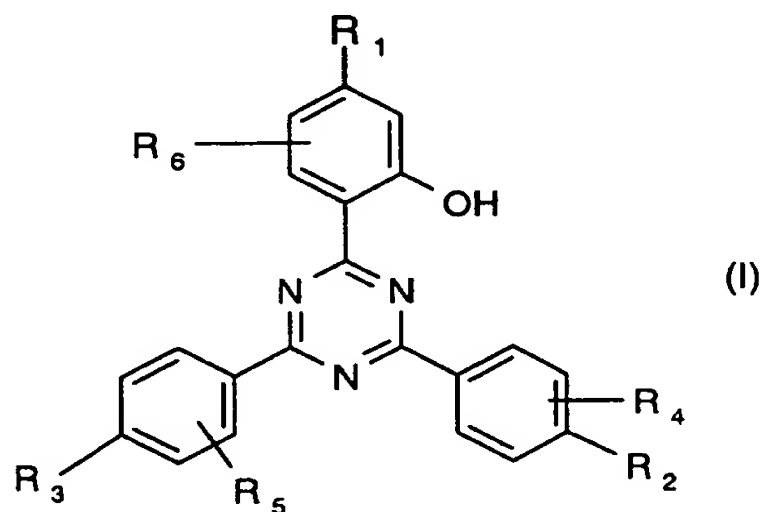
Transparent Polyolefin Articles of low Thickness

The invention relates to a novel polyolefin article of low thickness and good transparency having enhanced stability against the effects of light, oxygen, heat and aggressive chemicals, which is also effective as a selective UV filter for agricultural applications, and to some novel stabilizers suitable for this application.

Certain polyolefin articles containing UV absorbers of the type hydroxyphenyl triazine are known from GB-A-2319523, EP-A-704437, EP-A-704560, WO 99/57189.

Present invention pertains to a transparent polyolefin article stabilized by addition of 0.005-0.30 % by weight the polyolefin of a hydroxyphenyl triazine UV absorber, characterized in that the article has a thickness between 1 and 500 μm .

Preferred articles contain as a hydroxyphenyl triazine UV absorber a compound of the formula I



wherein

R_1 is H or OR_7 ;

R_2 and R_3 independently are H, , OR_9 ;

R_4 and R_5 independently are H, $\text{C}_1\text{-C}_8$ alkyl, OR_{10} ;

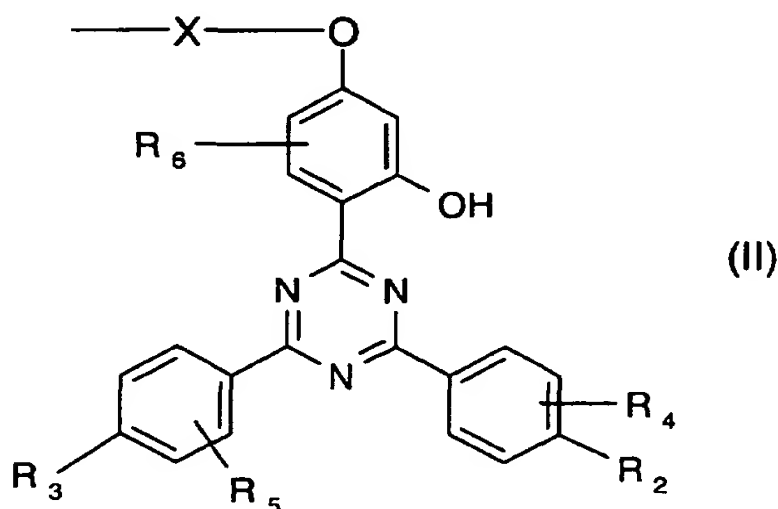
R_6 is H, $\text{C}_1\text{-C}_{18}$ alkyl, $\text{C}_5\text{-C}_{12}$ cycloalkyl, $\text{C}_7\text{-C}_{12}$ phenylalkyl, $\text{C}_7\text{-C}_{12}$ alkylphenyl, $\text{C}_3\text{-C}_{12}$ alkenyl, halogen, OH, OR_9 ;

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R_8 is H; halogen; C_1 - C_{12} alkoxy; C_1 - C_{12} alkyl; C_3 - C_{24} alkyl interrupted by oxygen and/or substituted by OH; or is $NH-CO-R_{14}$ or $NH-COO-R_{12}$;

R_7 , R_9 and R_{10} independently are H; C_1 - C_{24} alkyl; C_3 - C_{12} alkenyl; C_3 - C_{24} alkyl interrupted by oxygen and/or substituted by OH; or is C_5 - C_{12} cycloalkyl, C_7 - C_{12} phenylalkyl, C_7 - C_{12} alkylphenyl; $CH_2CH(OH)CH_2OR_{11}$; C_1 - C_{12} alkyl substituted by $COOR_{12}$, $CONR_{13}R_{14}$, $OCOR_{15}$, OH or halogen;

and R_7 also embraces a residue of formula II



wherein X is C_2 - C_{24} alkylene; $-CH_2CH(OH)CH_2-$; $-CH_2CH(OH)CH_2O-D-OCH_2CH(OH)CH_2-$; $(C_1-C_{18}alkylene)-CO-O-D-O-CO-(C_1-C_{18}alkylene)$; CO; $CO-(C_2-C_{24}alkylene)-CO$; C_3 - C_{24} alkylene interrupted by oxygen, e.g. $CH_2CH_2-O-CH_2CH_2$;

D is C_2 - C_{12} alkylene; C_4 - C_{50} alkylene interrupted by O; phenylene; biphenylene or phenylene-E-phenylene;

E is O, S, SO_2 ; CH_2 ; CO or $-C(CH_3)_2-$;

R_{11} is H, C_1 - C_{12} alkyl; phenyl; phenyl substituted by 1-3 C_1 - C_4 alkyl; C_5 - C_{12} cycloalkyl; C_7 - C_{12} phenylalkyl; C_3 - C_{12} alkenyl;

R_{12} is H; C_1 - C_{24} alkyl; C_3 - C_{12} alkenyl; C_3 - C_{36} alkyl interrupted by oxygen and/or substituted by OH; or is C_5 - C_{12} cycloalkyl, C_7 - C_{12} phenylalkyl, C_7 - C_{12} alkylphenyl; phenyl;

R_{13} and R_{14} independently are H, C_1 - C_{18} alkyl; phenyl; phenyl substituted by 1-3 C_1 - C_4 alkyl and/or C_1 - C_4 alkoxy; C_5 - C_{12} cycloalkyl; C_3 - C_{12} alkenyl;

R_{15} is C_1 - C_{12} alkyl; phenyl; phenyl substituted by 1-3 C_1 - C_4 alkyl and/or C_1 - C_4 alkoxy; C_5 - C_{12} cycloalkyl; C_3 - C_{12} alkenyl; C_1 - C_{12} alkoxy; or is $NR_{13}R_{14}$.

More preferably, in the hydroxyphenyl triazine UV absorber of the formula I

R_4 and R_5 and R_6 independently are H;

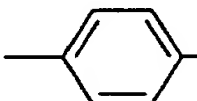
R_8 is H; C_1 - C_8 alkoxy; C_1 - C_8 alkyl;

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R_7, R_9 independently are H; C_1 - C_{18} alkyl; C_3 - C_{12} alkenyl; C_3 - C_{24} alkyl interrupted by oxygen and/or substituted by OH; or is C_5 - C_{12} cycloalkyl, C_7 - C_{12} phenylalkyl, C_7 - C_{12} alkylphenyl; C_1 - C_{12} alkyl substituted by $COOR_{12}$, $OCOR_{15}$, OH;
 and R_7 also embraces a residue of formula II, wherein X is C_2 - C_{18} alkylene; $-CH_2CH(OH)CH_2-$; $-CH_2CH(OH)CH_2O-D-OCH_2CH(OH)CH_2-$; $(C_1-C_4$ alkylene)- $CO-O-D-O-CO-(C_1-C_4$ alkylene); CO; $CO-(C_2-C_{18}$ alkylene)-CO; C_3 - C_{18} alkylene interrupted by oxygen;
 D is C_2 - C_{12} alkylene;
 R_{12} is H; C_1 - C_{24} alkyl; C_3 - C_{12} alkenyl; C_3 - C_{24} alkyl interrupted by oxygen and/or substituted by OH; or is C_5 - C_{12} cycloalkyl, C_7 - C_{12} phenylalkyl, C_7 - C_{12} alkylphenyl; phenyl;
 R_{15} is C_1 - C_{12} alkyl; C_5 - C_{12} cycloalkyl; C_3 - C_{12} alkenyl;

especially

R_1 is OR_7 ;

R_2 and R_3 independently are  R_8 , OR_9 ;

R_4 and R_5 and R_6 are H;

R_8 is H; C_1 - C_8 alkoxy; C_1 - C_4 alkyl;

R_7, R_9 independently are C_4 - C_{18} alkyl or C_5 - C_{12} cycloalkyl;

and R_7 also embraces a residue of formula II, wherein X is C_4 - C_{18} alkylene.

Of utmost importance are compounds of the formula I, wherein R_1 is OR_7 ; R_2 and R_3 each are phenyl; R_4, R_5 and R_6 are hydrogen; and R_7 is C_4 - C_{18} alkyl or C_5 - C_{12} cycloalkyl or a residue of formula II, wherein X is C_4 - C_{12} alkylene.

A halogen substituent is -F, -Cl, -Br or -I, preferably -F, -Cl or -Br and, in particular, -Cl.

Alkylphenyl is alkyl-substituted phenyl; C_7 - C_{14} alkylphenyl embraces examples such as methylphenyl (tolyl), dimethylphenyl (xylyl), trimethylphenyl (mesityl), ethylphenyl, propylphenyl, butylphenyl, dibutylphenyl, pentylphenyl, hexylphenyl, heptylphenyl and octylphenyl.

Phenylalkyl is phenyl-substituted alkyl; C_7 - C_{11} phenylalkyl embraces examples such as benzyl, α -methylbenzyl, α -ethylbenzyl, α, α -dimethylbenzyl, phenylethyl, phenylpropyl,

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phenylbutyl and phenylpentyl.

n-alkyl or alkyl-n is an unbranched alkyl radical.

Alkyl interrupted by O, NH, NR₁₃, etc., can generally comprise one or more nonadjacent heteroatoms. Preferably, a carbon atom of the alkyl chain bonds to not more than 1 heteroatom. R₇, R₉ and R₁₀, especially R₇, as alkyl substituted by COOR₁₂ is most preferably CH₂-COOR₁₂. R₁₂ is most preferably C₁-C₁₈alkyl, or C₆-C₁₂cycloalkyl; cycloalkyl is most preferably cyclohexyl or cyclododecyl.

Within the scope of the stated definitions, the radicals R₄, R₅, R₆, R₈, R₉, R₁₁, R₁₂, R₁₃, R₁₄, R₁₅ as alkyl are branched or unbranched alkyl such as methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, isobutyl, t-butyl, 2-ethylbutyl, n-pentyl, isopentyl, 1-methylpentyl, 1,3-dimethylbutyl, n-hexyl, 1-methylhexyl, n-heptyl, isoheptyl, 1,1,3,3-tetramethylbutyl, 1-methylheptyl, 3-methylheptyl, n-octyl, 2-ethylhexyl, 1,1,3-trimethylhexyl, 1,1,3,3-tetramethylpentyl, nonyl, decyl, undecyl, 1-methylundecyl, dodecyl, 1,1,3,3,5,5-hexamethylhexyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl and octadecyl.

C₁-C₄alkyl is especially methyl, ethyl, isopropyl, n-butyl, 2-butyl, 2-methylpropyl or tert-butyl.

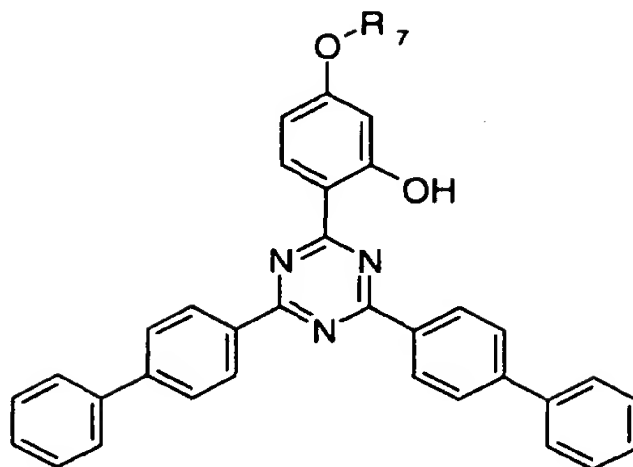
Within the scope of the stated definitions, R₄, R₅, R₆, R₈, R₉, R₁₁, R₁₂, R₁₃, R₁₄, R₁₅ as alkenyl include allyl, isopropenyl, 2-butenyl, 3-butenyl, isobutenyl, n-penta-2,4-dienyl, 3-methyl-but-2-enyl.

R₄, R₅ and R₆ are most preferably hydrogen. R₂ and R₃ are most preferably phenyl or OR₉, especially phenyl. R₉ is most preferably C₁-C₄alkyl.

Examples for highly effective compounds of the formula I are as listed in the following tables:

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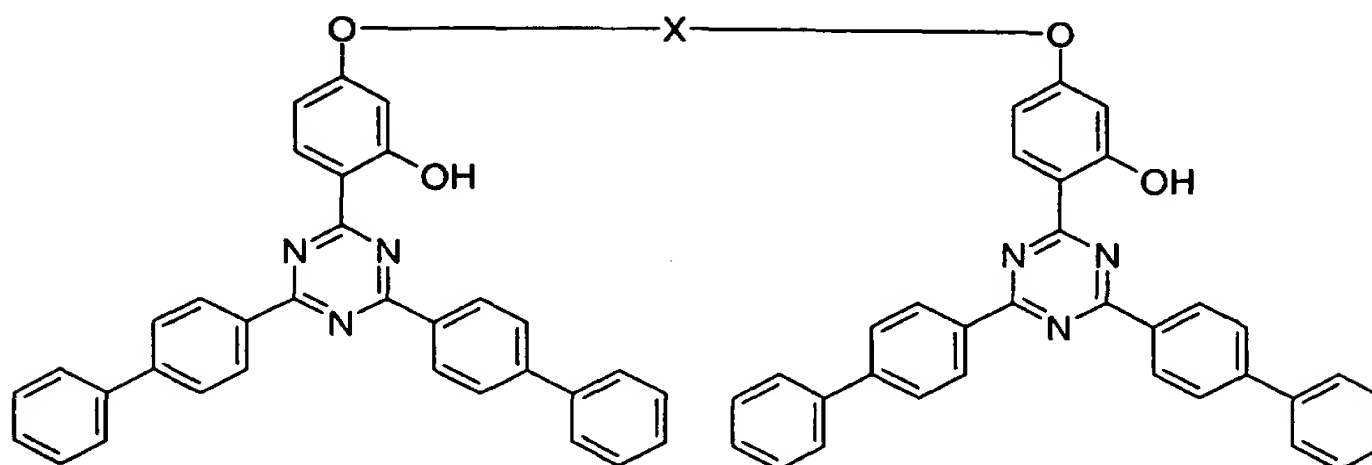
Table 1: Compounds of the formula



compound	R ₇
a)	CH ₂ CH(C ₂ H ₅)-(CH ₂) ₃ -CH ₃
b)	CH(CH ₃)-(CH ₂) ₉ -CH ₃
c)	n-C ₆ H ₁₃
d)	n-C ₈ H ₁₇
e)	n-C ₁₂ H ₂₅

In the above definitions, n denotes a straight alkyl chain.

Table 2: Compounds of the formula

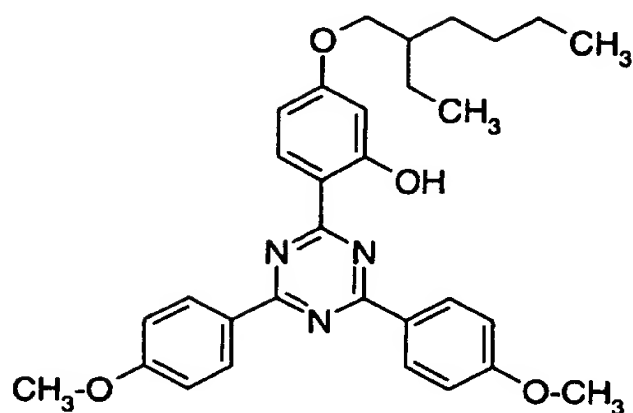


compound	X
f)	-(CH ₂) ₁₂ -
g)	-(CH ₂) ₁₀ -

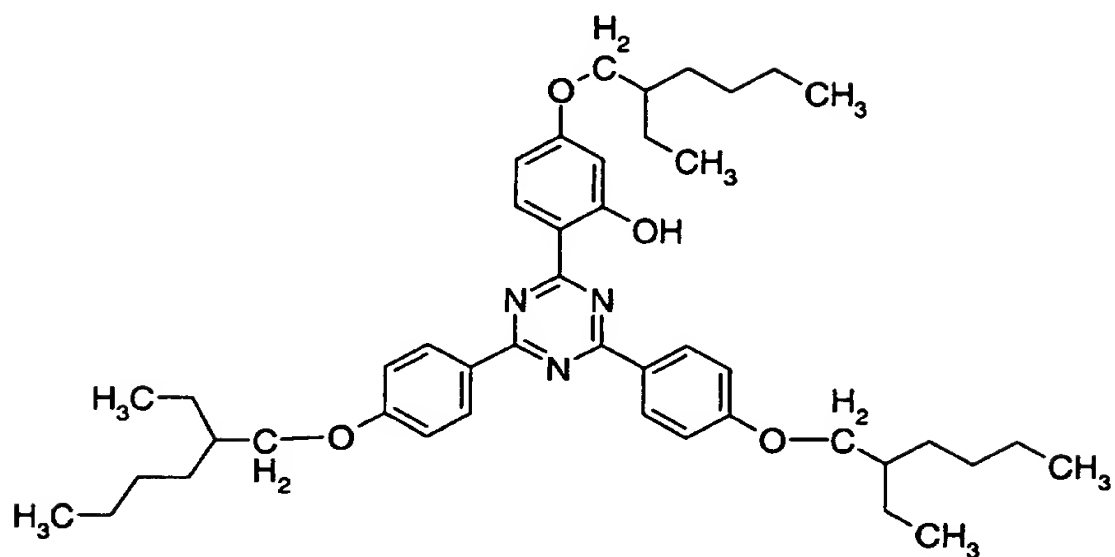
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Further examples for highly effective compounds of the formula I are the compounds

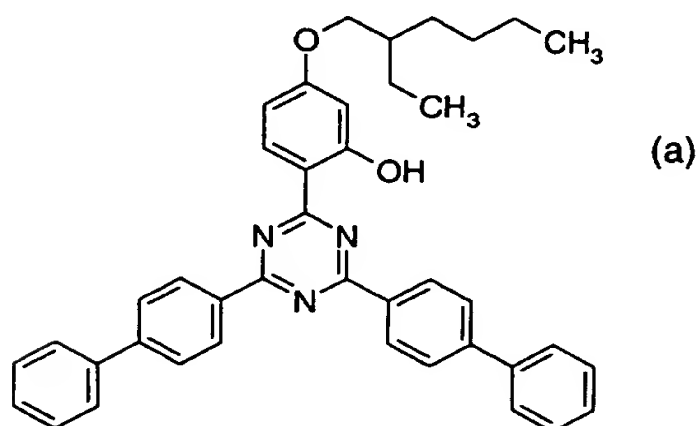
h)



i)



Some compounds of formula I are known, e.g. from WO 96/28431, US-5591850, EP-A-434608; others, e.g. the compounds



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as well as (b), (f) and (g) are novel compounds. They are conveniently prepared in analogy to procedures described in these references, especially to the method given in example 18 of WO 96/28431.

A particular useful application of polyolefin films of present invention is their use as greenhouse films. Some types of crops are degraded by the UV-components of solar radiation which must be filtered off to obtain high quality and productivity of the crops. Additionally, some microorganisms, e.g. *Botrytis Cinerea*, as well as some harmful insects, e.g. white flies, aphides, thrips or leafminers, can proliferate under specific UV-irradiation. These pest can be significantly reduced when UV light does not or to less extent reach the plants. [R. Reuveni et al., *Development of photoselective PE films for control of foliar pathogens in greenhouse-grown crops, Plasticulture No. 102, p. 7 (1994)*; Y. Antignus et al., *The use of UV absorbing plastic sheets to protect crops against insects and spread of virus diseases, CIPA Congress March 1997, pp.23-33*]. On the other hand, bee activity, requiring a certain band of UV radiation, needs to be retained in greenhouses in order to ensure fructification on flowering plants, e.g. tomato, cucumber, pumpkin etc.

Present hydroxyphenyl triazine UV absorbers show excellent compatibility and persistence in the polyolefin. The same time, these UV absorbers provide efficient and selective UV shielding for suppressing microbial growth in a protected environment, especially a plant cultivation, while retaining the UV irradiation necessary for bee activity. Thus, present invention also pertains to the use of a transparent polyolefin film as described above for suppressing microbial growth in a protected cultivation.

Examples for polyolefines to be used for manufacturing the articles of present invention include the following polymers:

1. Polymers of monoolefins and diolefins, for example polypropylene, polyisobutylene, polybut-1-ene, poly-4-methylpent-1-ene, polyisoprene or polybutadiene, as well as polymers of cycloolefins, for instance of cyclopentene or norbornene, polyethylene (which optionally can be crosslinked), for example high density polyethylene (HDPE), high density and high molecular weight polyethylene (HDPE-HMW), high density and ultrahigh molecular weight polyethylene (HDPE-UHMW), medium density polyethylene (MDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), (VLDPE) and (ULDPE).

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Polyolefins, i.e. the polymers of monoolefins exemplified in the preceding paragraph, preferably polyethylene and polypropylene, can be prepared by different, and especially by the following, methods:

- a) radical polymerisation (normally under high pressure and at elevated temperature).
- b) catalytic polymerisation using a catalyst that normally contains one or more than one metal of groups IVb, Vb, VIb or VIII of the Periodic Table. These metals usually have one or more than one ligand, typically oxides, halides, alcoholates, esters, ethers, amines, alkyls, alkenyls and/or aryls that may be either π - or σ -coordinated. These metal complexes may be in the free form or fixed on substrates, typically on activated magnesium chloride, titanium(III) chloride, alumina or silicon oxide. These catalysts may be soluble or insoluble in the polymerisation medium. The catalysts can be used by themselves in the polymerisation or further activators may be used, typically metal alkyls, metal hydrides, metal alkyl halides, metal alkyl oxides or metal alkyloxanes, said metals being elements of groups Ia, IIa and/or IIIa of the Periodic Table. The activators may be modified conveniently with further ester, ether, amine or silyl ether groups. These catalyst systems are usually termed Phillips, Standard Oil Indiana, Ziegler (-Natta), TNZ (DuPont), metallocene or single site catalysts (SSC).

2. Mixtures of the polymers mentioned under 1), for example mixtures of polypropylene with polyisobutylene, polypropylene with polyethylene (for example PP/HDPE, PP/LDPE) and mixtures of different types of polyethylene (for example LDPE/HDPE).

3. Polyolefin copolymers: Copolymers of monoolefins and diolefins with each other or with other vinyl monomers, for example ethylene/propylene copolymers, linear low density polyethylene (LLDPE) and mixtures thereof with low density polyethylene (LDPE), propylene/but-1-ene copolymers, propylene/isobutylene copolymers, ethylene/but-1-ene copolymers, ethylene/hexene copolymers, ethylene/methylpentene copolymers, ethylene/heptene copolymers, ethylene/octene copolymers, propylene/butadiene copolymers, isobutylene/isoprene copolymers, ethylene/alkyl acrylate copolymers, ethylene/alkyl methacrylate copolymers, ethylene/vinyl acetate copolymers and their copolymers with carbon monoxide or ethylene/acrylic acid copolymers and their salts (ionomers) as well as terpolymers of ethylene with propylene and a diene such as

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hexadiene, dicyclopentadiene or ethylidene-norbornene; and mixtures of such copolymers with one another and with polymers mentioned in 1) above, for example polypropylene/ethylene-propylene copolymers, LDPE/ethylene-vinyl acetate copolymers (EVA), LDPE/ethylene-acrylic acid copolymers (EAA), LLDPE/EVA, LLDPE/EAA and alternating or random polyalkylene/carbon monoxide copolymers and mixtures thereof with other polymers, for example polyamides.

Most preferred are polyethylene, especially LDPE or LLDPE, or polypropylene.

The transparent polyolefin article of the invention usually is a film, fiber, ribbon or stretched tape, especially an agricultural film. Its thickness preferably ranges between 1 and 300 μm , especially between 1 and 200 μm . The transparent polyolefin article of the invention often contains one or more further components, e.g. selected from further light stabilizers, processing stabilizers, fillers, clarifiers, modifiers, acid scavengers or other additives known in the art. For sufficient transparency, present articles do not contain crystalline components in an amount that would significantly impair this property; preferably they contain no pigments and no or merely minor amounts, e.g. 0 - 5 % by weight of the polymer, of fillers or crystalline inorganic components having lower opaquing effect than pigments (e.g. hydrotalcites). Examples for additional components which may be contained in the polymer articles of the invention include the following:

1. Antioxidants

1.1. Alkylated monophenols, for example 2,6-di-tert-butyl-4-methylphenol, 2-tert-butyl-4,6-dimethylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,6-di-tert-butyl-4-n-butylphenol, 2,6-di-tert-butyl-4-isobutylphenol, 2,6-dicyclopentyl-4-methylphenol, 2-(α -methylcyclohexyl)-4,6-dimethylphenol, 2,6-dioctadecyl-4-methylphenol, 2,4,6-tricyclohexylphenol, 2,6-di-tert-butyl-4-methoxymethylphenol, nonylphenols which are linear or branched in the side chains, for example 2,6-di-nonyl-4-methylphenol, 2,4-dimethyl-6-(1'-methylundec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methylheptadec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methyltridec-1'-yl)phenol and mixtures thereof.

1.2. Alkylthiomethylphenols, for example 2,4-dioctylthiomethyl-6-tert-butylphenol, 2,4-dioctylthiomethyl-6-methylphenol, 2,4-dioctylthiomethyl-6-ethylphenol, 2,6-di-dodecylthiomethyl-4-nonylphenol.

1.3. Hydroquinones and alkylated hydroquinones, for example 2,6-di-tert-butyl-4-methoxyphenol, 2,5-di-tert-butylhydroquinone, 2,5-di-tert-amylhydroquinone, 2,6-diphenyl-4-octadecyloxyphenol, 2,6-di-tert-butylhydroquinone, 2,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyphenyl stearate, bis(3,5-di-tert-butyl-4-hydroxyphenyl) adipate.

1.4. Tocopherols, for example α -tocopherol, β -tocopherol, γ -tocopherol, δ -tocopherol and mixtures thereof (vitamin E).

1.5. Hydroxylated thiodiphenyl ethers, for example 2,2'-thiobis(6-tert-butyl-4-methylphenol), 2,2'-thiobis(4-octylphenol), 4,4'-thiobis(6-tert-butyl-3-methylphenol), 4,4'-thiobis(6-tert-butyl-2-methylphenol), 4,4'-thiobis(3,6-di-sec-amylphenol), 4,4'-bis(2,6-dimethyl-4-hydroxyphenyl)-disulfide.

1.6. Alkylidenebisphenols, for example 2,2'-methylenebis(6-tert-butyl-4-methylphenol), 2,2'-methylenebis(6-tert-butyl-4-ethylphenol), 2,2'-methylenebis[4-methyl-6-(α -methylcyclohexyl)-phenol], 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 2,2'-methylenebis(6-nonyl-4-methylphenol), 2,2'-methylenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(6-tert-butyl-4-isobutylphenol), 2,2'-methylenebis[6-(α -methylbenzyl)-4-nonylphenol], 2,2'-methylenebis[6-(α,α -dimethylbenzyl)-4-nonylphenol], 4,4'-methylenebis(2,6-di-tert-butylphenol), 4,4'-methylenebis(6-tert-butyl-2-methylphenol), 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 2,6-bis(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol, 1,1,3-tris(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-3-n-dodecylmercaptobutane, ethylene glycol bis[3,3-bis(3'-tert-butyl-4'-hydroxyphenyl)butyrate], bis(3-tert-butyl-4-hydroxy-5-methyl-phenyl)dicyclopentadiene, bis[2-(3'-tert-butyl-2'-hydroxy-5'-methylbenzyl)-6-tert-butyl-4-methylphenyl]terephthalate, 1,1-bis-(3,5-dimethyl-2-hydroxyphenyl)butane, 2,2-bis(3,5-di-tert-butyl-4-hydroxyphenyl)propane, 2,2-bis-(5-tert-butyl-4-hydroxy-2-methylphenyl)-4-n-dodecylmercaptobutane, 1,1,5,5-tetra(5-tert-butyl-4-hydroxy-2-methylphenyl)pentane.

1.7. O-, N- and S-benzyl compounds, for example 3,5,3',5'-tetra-tert-butyl-4,4'-dihydroxydibenzyl ether, octadecyl-4-hydroxy-3,5-dimethylbenzylmercaptoacetate, tridecyl-4-hydroxy-3,5-di-tert-butylbenzylmercaptoacetate, tris(3,5-di-tert-butyl-4-hydroxybenzyl)amine, bis(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)dithioterephthalate, bis(3,5-di-tert-butyl-4-hydroxybenzyl)sulfide, isooctyl-3,5-di-tert-butyl-4-hydroxybenzylmercaptoacetate.

1.8. Hydroxybenzylated malonates, for example dioctadecyl-2,2-bis(3,5-di-tert-butyl-2-hydroxybenzyl)malonate, di-octadecyl-2-(3-tert-butyl-4-hydroxy-5-methylbenzyl)malonate, didodecylmercaptoethyl-2,2-bis(3,5-di-tert-butyl-4-hydroxybenzyl)malonate, bis[4-(1,1,3,3-tetramethylbutyl)phenyl]-2,2-bis(3,5-di-tert-butyl-4-hydroxybenzyl)malonate.

1.9. Aromatic hydroxybenzyl compounds, for example 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, 1,4-bis(3,5-di-tert-butyl-4-hydroxybenzyl)-2,3,5,6-tetramethylbenzene, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)phenol.

1.10. Triazine compounds, for example 2,4-bis(octylmercapto)-6-(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,3,5-triazine, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,2,3-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)isocyanurate, 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)isocyanurate, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenylethyl)-1,3,5-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)-hexahydro-1,3,5-triazine, 1,3,5-tris(3,5-dicyclohexyl-4-hydroxybenzyl)isocyanurate.

1.11. Benzylphosphonates, for example dimethyl-2,5-di-tert-butyl-4-hydroxybenzylphosphonate, diethyl-3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl-3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl-5-tert-butyl-4-hydroxy-3-methylbenzylphosphonate, the calcium salt of the monoethyl ester of 3,5-di-tert-butyl-4-hydroxybenzylphosphonic acid.

1.12. Acylaminophenols, for example 4-hydroxylauranilide, 4-hydroxystearanilide, octyl N-(3,5-di-tert-butyl-4-hydroxyphenyl)carbamate.

1.13. Esters of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, n-octanol, i-octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethy-

lene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

1.14. Esters of β -(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, n-octanol, i-octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane; 3,9-bis[2-{3-(3-tert-butyl-4-hydroxy-5-methylphenyl)propionyloxy}-1,1-dimethylethyl]-2,4,8,10-tetraoxaspiro[5.5]-undecane.

1.15. Esters of β -(3,5-dicyclohexyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

1.16. Esters of 3,5-di-tert-butyl-4-hydroxyphenyl acetic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

1.17. Amides of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid e.g. N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexamethylenediamide, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)trimethylenediamide, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazide, N,N'-bis[2-(3-[3,5-di-tert-butyl-4-hydroxyphenyl]propionyloxy)ethyl]oxamide (Nau-gard®XL-1, supplied by Uniroyal).

1.18. Ascorbic acid (vitamin C)

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1.19. Aminic antioxidants, for example N,N'-di-isopropyl-p-phenylenediamine, N,N'-di-sec-butyl-p-phenylenediamine, N,N'-bis(1,4-dimethylpentyl)-p-phenylenediamine, N,N'-bis(1-ethyl-3-methylpentyl)-p-phenylenediamine, N,N'-bis(1-methylheptyl)-p-phenylenediamine, N,N'-dicyclohexyl-p-phenylenediamine, N,N'-diphenyl-p-phenylenediamine, N,N'-bis(2-naphthyl)-p-phenylenediamine, N-isopropyl-N'-phenyl-p-phenylenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine, N-(1-methylheptyl)-N'-phenyl-p-phenylenediamine, N-cyclohexyl-N'-phenyl-p-phenylenediamine, 4-(p-toluenesulfamoyl)diphenylamine, N,N'-dimethyl-N,N'-di-sec-butyl-p-phenylenediamine, diphenylamine, N-allyldiphenylamine, 4-isopropoxydiphenylamine, N-phenyl-1-naphthylamine, N-(4-tert-octylphenyl)-1-naphthylamine, N-phenyl-2-naphthylamine, octylated diphenylamine, for example p,p'-di-tert-octyldiphenylamine, 4-n-butylaminophenol, 4-butyrylaminophenol, 4-nonanoylaminophenol, 4-dodecanoylaminophenol, 4-octadecanoylaminophenol, bis(4-methoxyphenyl)amine, 2,6-di-tert-butyl-4-dimethylaminomethylphenol, 2,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, N,N,N',N'-tetramethyl-4,4'-diaminodiphenylmethane, 1,2-bis[(2-methylphenyl)amino]ethane, 1,2-bis(phenylamino)propane, (o-tolyl)biguanide, bis[4-(1',3'-dimethylbutyl)phenyl]amine, tert-octylated N-phenyl-1-naphthylamine, a mixture of mono- and dialkylated tert-butyl/tert-octyldiphenylamines, a mixture of mono- and dialkylated nonyldiphenylamines, a mixture of mono- and dialkylated dodecyldiphenylamines, a mixture of mono- and dialkylated isopropyl/isohexyldiphenylamines, a mixture of mono- and dialkylated tert-butyldiphenylamines, 2,3-dihydro-3,3-dimethyl-4H-1,4-benzothiazine, phenothiazine, a mixture of mono- and dialkylated tert-butyl/tert-octylphenothiazines, a mixture of mono- and dialkylated tert-octylphenothiazines, N-allylphenothiazine, N,N,N',N'-tetraphenyl-1,4-diaminobut-2-ene, N,N-bis(2,2,6,6-tetramethyl-piperid-4-yl-hexamethylenediamine, bis(2,2,6,6-tetramethylpiperid-4-yl)-sebacate, 2,2,6,6-tetramethylpiperidin-4-one, 2,2,6,6-tetramethylpiperidin-4-ol.

2. UV absorbers and light stabilisers

2.1. 2-(2'-Hydroxyphenyl)benzotriazoles, for example 2-(2'-hydroxy-5'-methylphenyl)benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(5'-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-5'-(1,1,3,3-tetramethylbutyl)phenyl)benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-methylphenyl)-5-chlorobenzotriazole, 2-(3'-sec-butyl-5'-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-4'-octyloxyphenyl)benzotriazole, 2-(3',5'-di-tert-amyl-2'-hydroxyphenyl)benzotriazole, 2-(3',5'-bis(α,α -dimethylbenzyl)-2'-hydroxyphenyl)benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-

(2-octyloxycarbonylethyl)phenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)carbonylethyl]-2'-hydroxyphenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonylethyl)phenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonylethyl)phenyl)benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxycarbonylethyl)phenyl)benzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)carbonylethyl]-2'-hydroxyphenyl)benzotriazole, 2-(3'-dodecyl-2'-hydroxy-5'-methylphenyl)benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-isooctyloxycarbonylethyl)phenyl)benzotriazole, 2,2'-methylenebis[4-(1,1,3,3-tetramethylbutyl)-6-benzotriazole-2-ylphenol]; the transesterification product of 2-[3'-tert-butyl-5'-(2-methoxycarbonylethyl)-2'-hydroxyphenyl]-2H-benzotriazole with polyethylene glycol 300; $\left[R - CH_2CH_2 - COO - CH_2CH_2 \right]_2$, where R = 3'-tert-butyl-4'-hydroxy-5'-2H-benzotriazol-2-ylphenyl, 2-[2'-hydroxy-3'-(α,α -dimethylbenzyl)-5'-(1,1,3,3-tetramethylbutyl)phenyl]-benzotriazole; 2-[2'-hydroxy-3'-(1,1,3,3-tetramethylbutyl)-5'-(α,α -dimethylbenzyl)phenyl]benzotriazole.

2.2. 2-Hydroxybenzophenones, for example the 4-hydroxy, 4-methoxy, 4-octyloxy, 4-decyloxy, 4-dodecyloxy, 4-benzyloxy, 4,2',4'-trihydroxy and 2'-hydroxy-4,4'-dimethoxy derivatives.

2.3. Esters of substituted and unsubstituted benzoic acids, for example 4-tert-butylphenyl salicylate, phenyl salicylate, octylphenyl salicylate, dibenzoyl resorcinol, bis(4-tert-butylbenzoyl)resorcinol, benzoyl resorcinol, 2,4-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate, hexadecyl 3,5-di-tert-butyl-4-hydroxybenzoate, octadecyl 3,5-di-tert-butyl-4-hydroxybenzoate, 2-methyl-4,6-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate.

2.4. Acrylates, for example ethyl α -cyano- β,β -diphenylacrylate, isooctyl α -cyano- β,β -diphenylacrylate, methyl α -carbomethoxycinnamate, methyl α -cyano- β -methyl-p-methoxycinnamate, butyl α -cyano- β -methyl-p-methoxycinnamate, methyl α -carbomethoxy-p-methoxycinnamate and N-(β -carbomethoxy- β -cyanovinyl)-2-methylindoline.

2.5. Nickel compounds, for example nickel complexes of 2,2'-thiobis[4-(1,1,3,3-tetramethylbutyl)phenol], such as the 1:1 or 1:2 complex, with or without additional ligands such as n-butylamine, triethanolamine or N-cyclohexyldiethanolamine, nickel dibutyldithiocarbamate, nickel salts of the monoalkyl esters, e.g. the methyl or ethyl ester, of 4-hydroxy-3,5-di-tert-butylbenzylphosphonic acid, nickel complexes of ketoximes, e.g. of 2-hydroxy-4-methylphe-

nylundecylketoxime, nickel complexes of 1-phenyl-4-lauroyl-5-hydroxypyrazole, with or without additional ligands.

2.6. Sterically hindered amines, for example bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate, bis(2,2,6,6-tetramethyl-4-piperidyl)succinate, bis(1,2,2,6,6-pentamethyl-4-piperidyl)sebacate, bis(1-octyloxy-2,2,6,6-tetramethyl-4-piperidyl)sebacate, bis(1,2,2,6,6-pentamethyl-4-piperidyl) n-butyl-3,5-di-tert-butyl-4-hydroxybenzylmalonate, the condensate of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid, linear or cyclic condensates of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-tert-octylamino-2,6-dichloro-1,3,5-triazine, tris(2,2,6,6-tetramethyl-4-piperidyl)nitrilotriacetate, tetrakis(2,2,6,6-tetramethyl-4-piperidyl)-1,2,3,4-butanetetracarboxylate, 1,1'-(1,2-ethanediyl)-bis(3,3,5,5-tetramethylpiperazinone), 4-benzoyl-2,2,6,6-tetramethylpiperidine, 4-stearyloxy-2,2,6,6-tetramethylpiperidine, bis(1,2,2,6,6-pentamethylpiperidyl)-2-n-butyl-2-(2-hydroxy-3,5-di-tert-butylbenzyl)-malonate, 3-n-octyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl)sebacate, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl)succinate, linear or cyclic condensates of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-morpholino-2,6-dichloro-1,3,5-triazine, the condensate of 2-chloro-4,6-bis(4-n-butylamino-2,2,6,6-tetramethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, the condensate of 2-chloro-4,6-di-(4-n-butylamino-1,2,2,6,6-pentamethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, 8-acetyl-3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione, 3-dodecyl-1-(2,2,6,6-tetramethyl-4-piperidyl)pyrrolidine-2,5-dione, 3-dodecyl-1-(1,2,2,6,6-pentamethyl-4-piperidyl)pyrrolidine-2,5-dione, a mixture of 4-hexadecyloxy- and 4-stearyloxy-2,2,6,6-tetramethylpiperidine, a condensate of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-cyclohexylamino-2,6-dichloro-1,3,5-triazine, a condensate of 1,2-bis(3-aminopropylamino)ethane and 2,4,6-trichloro-1,3,5-triazine as well as 4-butylamino-2,2,6,6-tetramethylpiperidine (CAS Reg. No. [136504-96-6]); a condensate of 1,6-hexanediamine and 2,4,6-trichloro-1,3,5-triazine as well as N,N-dibutylamine and 4-butylamino-2,2,6,6-tetramethylpiperidine (CAS Reg. No. [192268-64-7]); N-(2,2,6,6-tetramethyl-4-piperidyl)-n-dodecylsuccinimide, N-(1,2,2,6,6-pentamethyl-4-piperidyl)-n-dodecylsuccinimide, 2-undecyl-7,7,9,9-tetramethyl-1-oxa-3,8-diaza-4-oxo-spiro[4,5]decane, a reaction product of 7,7,9,9-tetramethyl-2-cycloundecyl-1-oxa-3,8-diaza-4-oxospiro-[4,5]decane and epichlorohydrin, 1,1-bis(1,2,2,6,6-pentamethyl-4-piperidyloxy-carbonyl)-2-(4-methoxyphenyl)ethene, N,N'-bis-formyl-N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine, a diester of 4-methoxymethylenemalonic acid with 1,2,2,6,6-pentamethyl-4-hydroxypiperidine, poly[methylpropyl-3-oxy-4-(2,2,6,6-tetramethyl-4-piperi-

diyl)siloxane, a reaction product of maleic acid anhydride- α -olefin copolymer with 2,2,6,6-tetramethyl-4-aminopiperidine or 1,2,2,6,6-pentamethyl-4-aminopiperidine.

2.7. Oxamides, for example 4,4'-dioctyloxyoxanilide, 2,2'-diethoxyoxanilide, 2,2'-dioctyloxy-5,5'-di-tert-butoxanilide, 2,2'-didodecyloxy-5,5'-di-tert-butoxanilide, 2-ethoxy-2'-ethyloxanilide, N,N'-bis(3-dimethylaminopropyl)oxamide, 2-ethoxy-5-tert-butyl-2'-ethoxanilide and its mixture with 2-ethoxy-2'-ethyl-5,4'-di-tert-butoxanilide, mixtures of o- and p-methoxy-disubstituted oxanilides and mixtures of o- and p-ethoxy-disubstituted oxanilides.

2.8. 2-(2-Hydroxyphenyl)-1,3,5-triazines, for example 2,4,6-tris(2-hydroxy-4-octyloxyphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2,4-dihydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2,4-bis(2-hydroxy-4-propyloxyphenyl)-6-(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(4-methylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-dodecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-tridecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-butyloxypropoxy)phenyl]-4,6-bis(2,4-dimethyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-octyloxypropyloxy)phenyl]-4,6-bis(2,4-dimethyl)-1,3,5-triazine, 2-[4-(dodecyloxy/tridecyloxy-2-hydroxypropoxy)-2-hydroxyphenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-dodecyloxypropoxy)phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-hexyloxy)phenyl-4,6-diphenyl-1,3,5-triazine, 2-(2-hydroxy-4-methoxyphenyl)-4,6-diphenyl-1,3,5-triazine, 2,4,6-tris[2-hydroxy-4-(3-butoxy-2-hydroxypropoxy)phenyl]-1,3,5-triazine, 2-(2-hydroxyphenyl)-4-(4-methoxyphenyl)-6-phenyl-1,3,5-triazine, 2-[2-hydroxy-4-[3-(2-ethylhexyl-1-oxy)-2-hydroxypropyloxy]phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine.

3. Metal deactivators, for example N,N'-diphenyloxamide, N-salicylal-N'-salicyloyl hydrazine, N,N'-bis(salicyloyl)hydrazine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazine, 3-salicyloylamino-1,2,4-triazole, bis(benzylidene)oxalyl dihydrazide, oxanilide, isophthaloyl dihydrazide, sebacoyl bisphenylhydrazide, N,N'-diacetyl adipoyl dihydrazide, N,N'-bis(salicyloyl)oxalyl dihydrazide, N,N'-bis(salicyloyl)thiopropionyl dihydrazide.

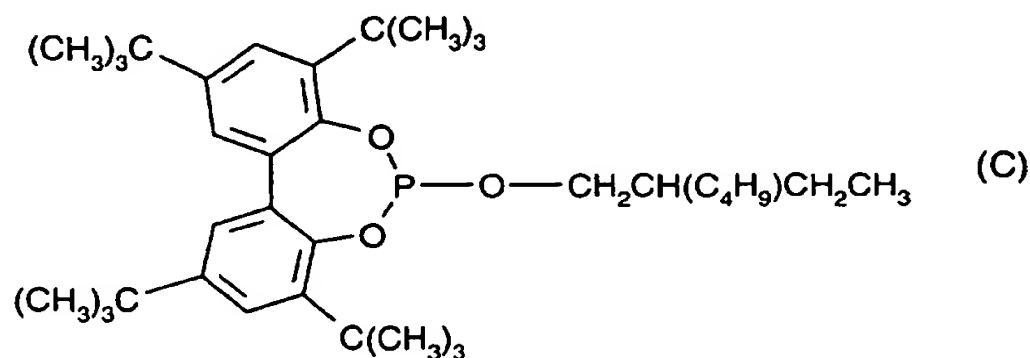
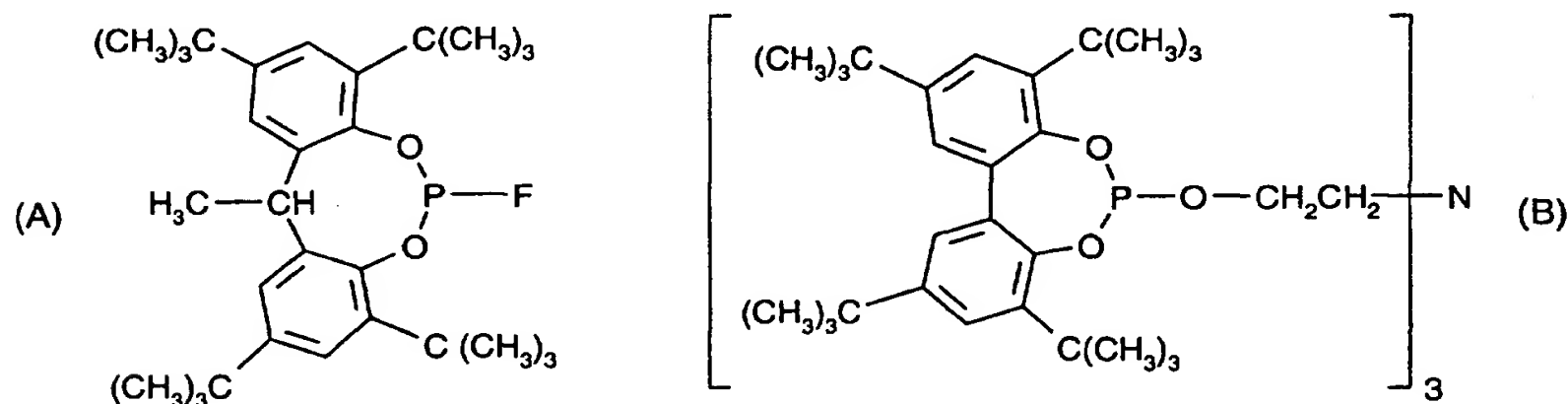
4. Phosphites and phosphonites, for example triphenyl phosphite, diphenylalkyl phosphites, phenyldialkyl phosphites, tris(nonylphenyl) phosphite, trilauryl phosphite, trioctadecyl phosphite, distearyl pentaerythritol diphosphite, tris(2,4-di-tert-butylphenyl) phosphite, diisodecyl pentaerythritol diphosphite, bis(2,4-di-tert-butylphenyl)pentaerythritol diphosphite, bis(2,4-di-

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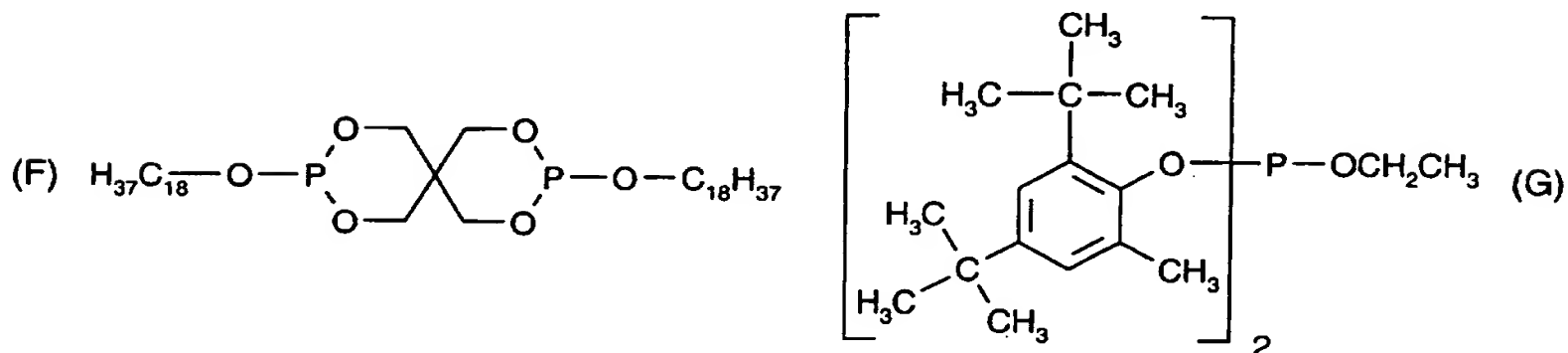
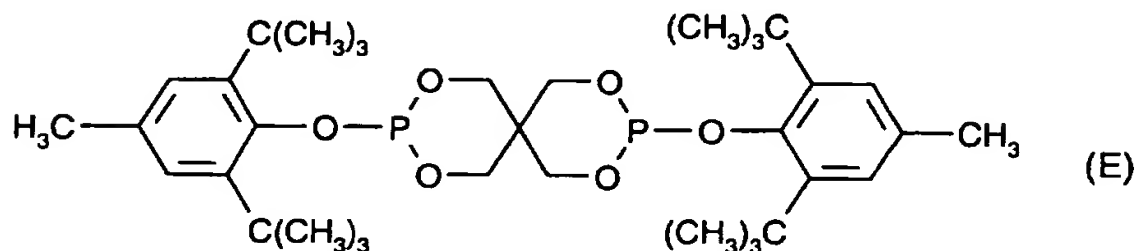
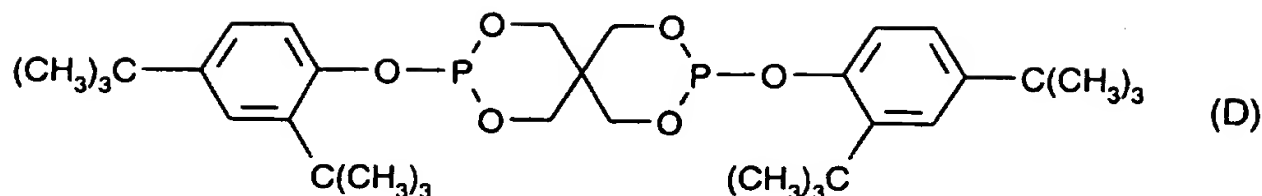
cumylphenyl)pentaerythritol diphosphite, bis(2,6-di-tert-butyl-4-methylphenyl)pentaerythritol diphosphite, diisodecyloxypentaerythritol diphosphite, bis(2,4-di-tert-butyl-6-methylphenyl)pentaerythritol diphosphite, bis(2,4,6-tris(tert-butylphenyl)pentaerythritol diphosphite, tristearyl sorbitol triphosphite, tetrakis(2,4-di-tert-butylphenyl) 4,4'-biphenylene diphosphonite, 6-isooctyloxy-2,4,8,10-tetra-tert-butyl-12H-dibenz[d,g]-1,3,2-dioxaphosphocin, bis(2,4-di-tert-butyl-6-methylphenyl)methyl phosphite, bis(2,4-di-tert-butyl-6-methylphenyl)ethyl phosphite, 6-fluoro-2,4,8,10-tetra-tert-butyl-12-methyl-dibenz[d,g]-1,3,2-dioxaphosphocin, 2,2',2''-nitrilo-[triethyltris(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl)phosphite], 2-ethylhexyl(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl)phosphite, 5-butyl-5-ethyl-2-(2,4,6-tri-tert-butylphenoxy)-1,3,2-dioxaphosphirane.

The following phosphites are especially preferred:

Tris(2,4-di-tert-butylphenyl) phosphite (Irgafos®168, Ciba-Geigy), tris(nonylphenyl) phosphite,



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5. Hydroxylamines, for example N,N-dibenzylhydroxylamine, N,N-diethylhydroxylamine, N,N-dioctylhydroxylamine, N,N-dilaurylhydroxylamine, N,N-ditetradecylhydroxylamine, N,N-dihexadecylhydroxylamine, N,N-dioctadecylhydroxylamine, N-hexadecyl-N-octadecylhydroxylamine, N-heptadecyl-N-octadecylhydroxylamine, N,N-dialkylhydroxylamine derived from hydrogenated tallow amine.

6. Nitrones, for example N-benzyl-alpha-phenylnitron, N-ethyl-alpha-methylnitron, N-octyl-alpha-heptylnitron, N-lauryl-alpha-undecylnitron, N-tetradecyl-alpha-tridecylnitron, N-hexadecyl-alpha-pentadecylnitron, N-octadecyl-alpha-heptadecylnitron, N-hexadecyl-alpha-heptadecylnitron, N-octadecyl-alpha-pentadecylnitron, N-heptadecyl-alpha-heptadecylnitron, N-octadecyl-alpha-hexadecylnitron, nitron derived from N,N-dialkylhydroxylamine derived from hydrogenated tallow amine.

7. Thiosynergists, for example dilauryl thiodipropionate or distearyl thiodipropionate.

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8. Peroxide scavengers, for example esters of β -thiodipropionic acid, for example the lauryl, stearyl, myristyl or tridecyl esters, mercaptobenzimidazole or the zinc salt of 2-mercaptobenzimidazole, zinc dibutyldithiocarbamate, dioctadecyl disulfide, pentaerythritol tetrakis(β -dodecylmercapto)propionate.

9. Polyamide stabilisers, for example copper salts in combination with iodides and/or phosphorus compounds and salts of divalent manganese.

10. Basic co-stabilisers, for example melamine, polyvinylpyrrolidone, dicyandiamide, triallyl cyanurate, urea derivatives, hydrazine derivatives, amines, polyamides, polyurethanes, alkali metal salts and alkaline earth metal salts of higher fatty acids, for example calcium stearate, zinc stearate, magnesium behenate, magnesium stearate, sodium ricinoleate and potassium palmitate, antimony pyrocatecholate or zinc pyrocatecholate.

11. Nucleating agents, for example inorganic substances, such as talcum, metal oxides, such as titanium dioxide or magnesium oxide, phosphates, carbonates or sulfates of, preferably, alkaline earth metals; organic compounds, such as mono- or polycarboxylic acids and the salts thereof, e.g. 4-tert-butylbenzoic acid, adipic acid, diphenylacetic acid, sodium succinate or sodium benzoate; polymeric compounds, such as ionic copolymers (ionomers). Especially preferred are 1,3:2,4-bis(3',4'-dimethylbenzylidene)sorbitol, 1,3:2,4-di(paramethyldibenzylidene)sorbitol, and 1,3:2,4-di(benzylidene)sorbitol.

12. Fillers and reinforcing agents, for example calcium carbonate, silicates, glass fibres, glass bulbs, asbestos, talc, kaolin, mica, barium sulfate, metal oxides and hydroxides, wood flour and flours or fibers of other natural products, synthetic fibers.

13. Other additives, for example plasticisers, lubricants, emulsifiers, pigments, rheology additives, catalysts, flow-control agents, flameproofing agents, antistatic agents and blowing agents.

14. Benzofuranones and indolinones, for example those disclosed in U.S. 4,325,863; U.S. 4,338,244; U.S. 5,175,312; U.S. 5,216,052; U.S. 5,252,643; DE-A-4316611; DE-A-4316622; DE-A-4316876; EP-A-0589839 or EP-A-0591102 or 3-[4-(2-acetoxyethoxy)-phenyl]-5,7-di-tert-butyl-benzofuran-2-one, 5,7-di-tert-butyl-3-[4-(2-stearoyloxyethoxy)phe-

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nyl]benzofuran-2-one, 3,3'-bis[5,7-di-tert-butyl-3-(4-[2-hydroxyethoxy]phenyl)benzofuran-2-one], 5,7-di-tert-butyl-3-(4-ethoxyphenyl)benzofuran-2-one, 3-(4-acetoxy-3,5-dimethylphenyl)-5,7-di-tert-butyl-benzofuran-2-one, 3-(3,5-dimethyl-4-pivaloyloxyphenyl)-5,7-di-tert-butyl-benzofuran-2-one, 3-(3,4-dimethylphenyl)-5,7-di-tert-butyl-benzofuran-2-one, 3-(2,3-dimethylphenyl)-5,7-di-tert-butyl-benzofuran-2-one.

The conventional additives are judiciously employed in amounts up to 10 % by weight, e.g. 0.1-10 % by weight, especially 0.2-5 % by weight, based on the material to be stabilized.

Acid scavengers may be added, especially in order to improve the lifetime of agricultural materials which come in contact with pesticides, e.g. greenhouse films. Components active as acid scavengers include metal oxides and/or hydroxides, e.g. oxides or hydroxides of zinc, magnesium, aluminum, calcium, mixed salts thereof, as well as hydrotalcites or zeolithes as described, for example, in GB-A-2300192, from page 2, line 2, until page 4, line 22.

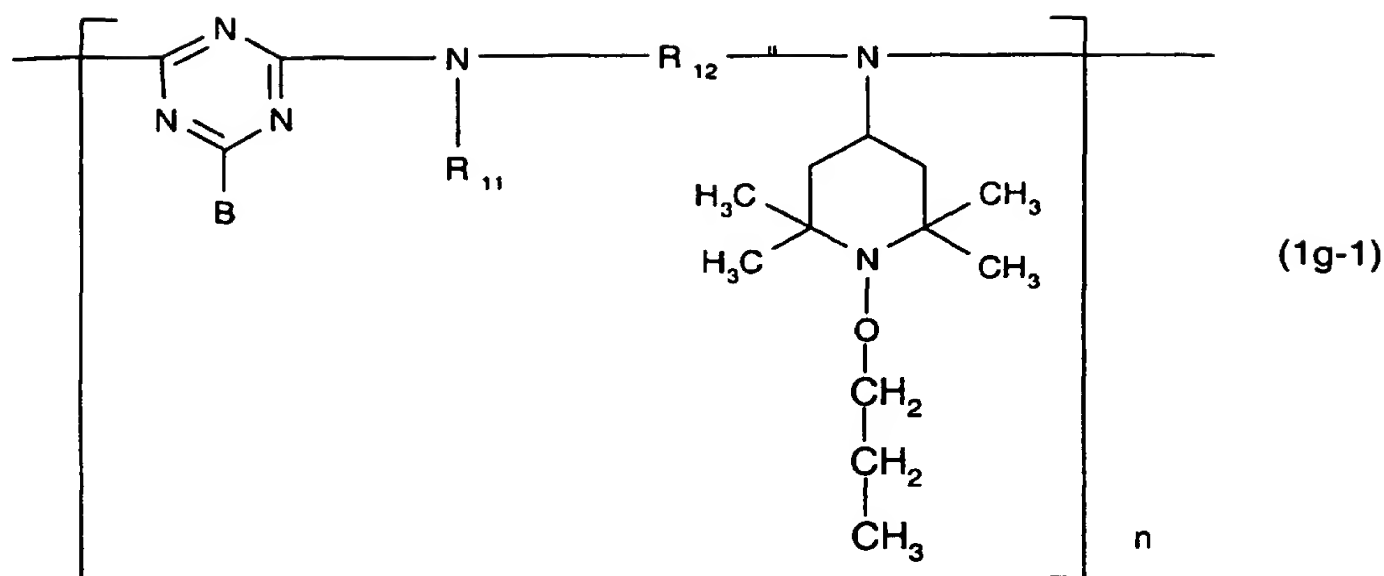
Thin-walled articles of the invention, especially transparent polyolefin agricultural films, act as a selective UV filter enhancing plant growth and crop while suppressing the undesired activity of microorganisms. Light of the medium or far UV region (e.g. 200-360 nm) required by these microorganisms is effectively blocked. The same time, the activity of useful insects such as bees is not affected.

Preferably, the transparent polyolefin article of the invention also contains a sterically hindered amine as further stabilizer in order to obtain optimum light stability of the substrate. The sterically hindered amine is usually contained in an amount of 0.01 - 6 % by weight the polyolefin, the weight ratio sterically hindered amine : hydroxyphenyl triazine UV absorber preferably ranging from 2 : 1 to 20 : 1.

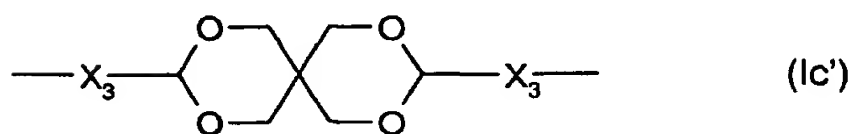
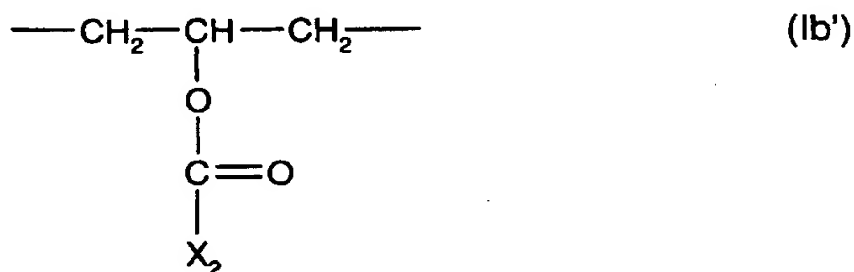
Examples for sterically hindered amines preferably contained in the polyolefin articles of the invention are given in the above list (item 2.6).

Best results are obtained with a sterically hindered amine from the class of the hydroxylamine ethers. Examples for the most preferred hydroxylamine ethers are compounds of the formula (1g-1)

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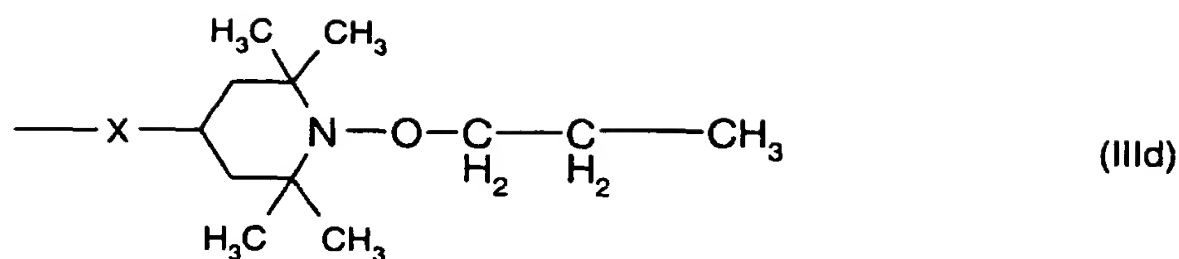
in which the index n ranges from 1 to 15, being especially from the range 3-9;
 R_{12} is C_2 - C_{12} alkylene, C_4 - C_{12} alkenylene, C_5 - C_7 cycloalkylene, C_5 - C_7 cycloalkylene-
 di(C_1 - C_4 alkylene), C_1 - C_4 alkylenedi(C_5 - C_7 cycloalkylene), phenylenedi(C_1 - C_4 alkylene) or
 C_4 - C_{12} alkylene interrupted by 1,4-piperazinediyl, -O- or $>N-X_1$ with X_1 being C_1 - C_{12} acyl or
 (C_1 - C_{12} alkoxy)carbonyl or having one of the definitions of R_{14} given below except hydrogen;
 or R_{12} is a group of the formula (lb') or (lc');



with m being 2 or 3,

X_2 being C_1 - C_{18} alkyl, C_5 - C_{12} cycloalkyl which is unsubstituted or substituted by 1, 2 or 3
 C_1 - C_4 alkyl; phenyl which is unsubstituted or substituted by 1, 2 or 3 C_1 - C_4 alkyl or
 C_1 - C_4 alkoxy; C_7 - C_9 phenylalkyl which is unsubstituted or substituted on the phenyl by 1, 2 or 3
 C_1 - C_4 alkyl; and
 the radicals X_3 being independently of one another C_2 - C_{12} alkylene;
 the radicals B are independently of one another Cl, $-OR_{13}$, $-N(R_{14})(R_{15})$ or a group of the
 formula (IIId);

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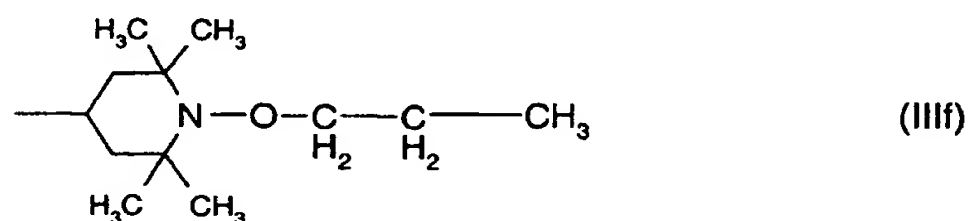


R_{13} , R_{14} and R_{15} , which are identical or different, are hydrogen, C_1 - C_{18} alkyl, C_5 - C_{12} cycloalkyl which is unsubstituted or substituted by 1, 2 or 3 C_1 - C_4 alkyl; C_3 - C_{18} alkenyl, phenyl which is unsubstituted or substituted by 1, 2 or 3 C_1 - C_4 alkyl or C_1 - C_4 alkoxy; C_7 - C_9 phenylalkyl which is unsubstituted or substituted on the phenyl by 1, 2 or 3 C_1 - C_4 alkyl; tetrahydrofurfuryl or C_2 - C_4 alkyl which is substituted in the 2, 3 or 4 position by -OH, C_1 - C_8 alkoxy, di(C_1 - C_4 alkyl)amino or a group of the formula (Ie');



with Y being -O-, -CH₂-, -CH₂CH₂- or >N-CH₃,
or -N(R_{14})(R_{15}) is additionally a group of the formula (Ie');
X is -O- or >N- R_{16} ;

R_{16} is hydrogen, C_1 - C_{18} alkyl, C_3 - C_{18} alkenyl, C_5 - C_{12} cycloalkyl which is unsubstituted or substituted by 1, 2 or 3 C_1 - C_4 alkyl; C_7 - C_9 phenylalkyl which is unsubstituted or substituted on the phenyl by 1, 2 or 3 C_1 - C_4 alkyl; tetrahydrofurfuryl, a group of the formula (IIIIf),

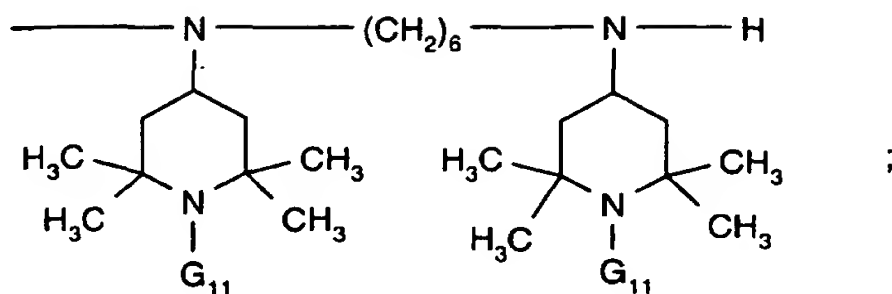


or C_2 - C_4 alkyl which is substituted in the 2, 3 or 4 position by -OH, C_1 - C_8 alkoxy, di(C_1 - C_4 alkyl)amino or a group of the formula (Ie');

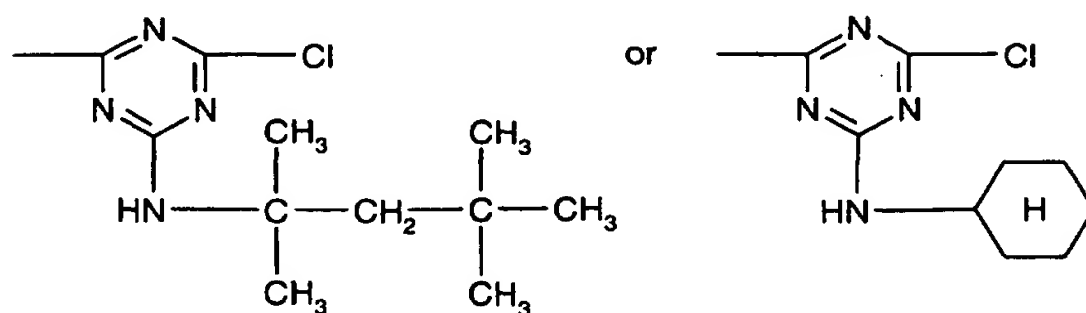
R_{11} has one of the definitions given for R_{16} .

In these compounds, the end group bonded to the triazine residue can be, for example, a group B or -N(R_{11})- R_{12} -B, such as chlorine or a group

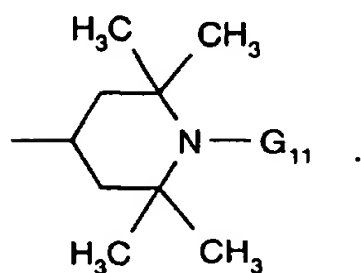
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and the end group bonded to the diamino group can be, for example, hydrogen or a di-B-substituted triazinyl group, such as a group



It may be convenient to replace the chlorine attached to the triazine by e.g. -OH or an amino group. Suitable amino groups are typically: pyrrolidin-1-yl, morpholino, -NH₂, -N(C₁-C₈alkyl)₂ and -NY'(C₁-C₈alkyl) wherein Y' is hydrogen or a group of the formula

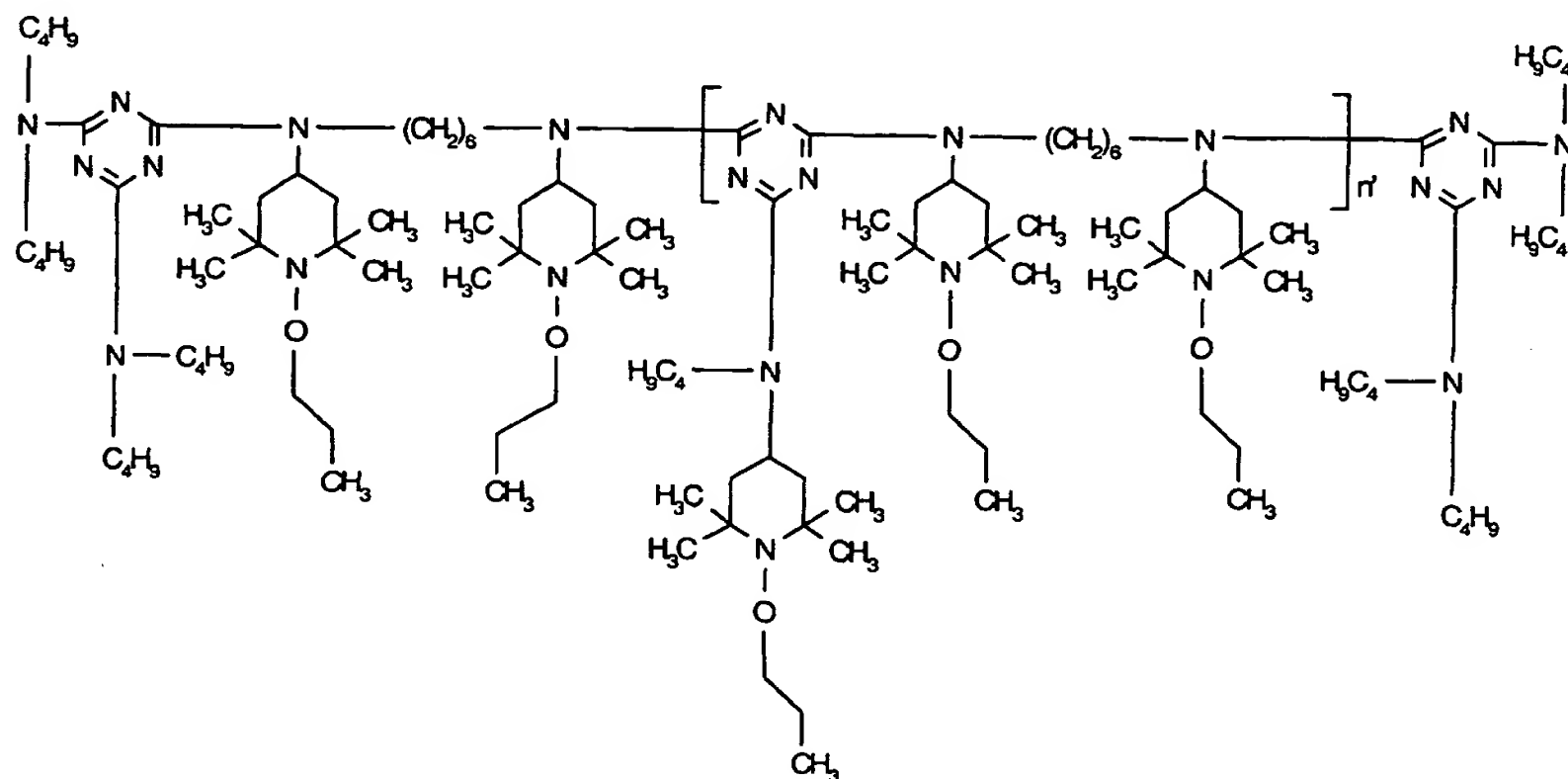


In the above shown oligomeric and polymeric compounds, examples of alkyl are methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, 2-ethylbutyl, n-pentyl, isopentyl, 1-methylpentyl, 1,3-dimethylbutyl, n-hexyl, 1-methylhexyl, n-heptyl, isoheptyl, 1,1,3,3-tetramethylbutyl, 1-methylheptyl, 3-methylheptyl, n-octyl, 2-ethylhexyl, 1,1,3-trimethylhexyl, 1,1,3,3-tetramethylpentyl, nonyl, decyl, undecyl, 1-methylundecyl, dodecyl, 1,1,3,3,5,5-hexamethylhexyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, eicosyl and docosyl;

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examples of cycloalkyl are cyclopentyl, cyclohexyl, cycloheptyl and cyclooctyl;
 an example of C₇-C₉phenylalkyl is benzyl; and
 examples of alkylene are ethylene, propylene, trimethylene, tetramethylene, pentamethylene, 2,2-dimethyltrimethylene, hexamethylene, trimethylhexamethylene, octamethylene and decamethylene.

An example for a highly effective compound of formula (1g-1) is the compound of the formula (1g-2)



wherein n' is approximately 3 (example 2 of GB-A-2334717, CAS # 247243-62-5, which is the NO-n-propyl derivative of the block oligomer Chimassorb® 2020 CAS # 192268-64-7, Ciba Specialty Chemicals Corp.).

Example 1: Combination hydroxyphenyl triazine compound (a) with compound (1g-2)

In order to evaluate the UV-absorber characteristics of hydroxyphenyl triazine compound (a), when mixed with a commercial thermoplastic material, thin low density polyethylene (LDPE) films are prepared, containing, as a typical formulation, 0.15% by weight of the above compound (a) and 0.70% of the sterically hindered amine ether (1g-2), used as light stabilizer of the polymeric system in highly demanding environments for agriculture applications. To do so, properly weighted amounts of the compounds are mixed with ground LDPE (Polimeri Europa, supplied by Enichem, Milano, Italy), characterized by a density of 0.921 g/cm³ and a melt flow index (190°C/2.16 kg) of 0.6 in a turbo mixer. The mixture is

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extruded at a maximum temperature of 200°C in a OMC[®] twin-screw extruder. The granules so obtained are blown in a lab scale Formac[®] blow-extruder at a maximum temperature of 210°C to give a film of 150 µm thickness.

UV-Vis spectrum of the film as-obtained is recorded in the range 200-800 nm by means of a Perkin-Elmer lambda[®] 20 spectrophotometer, equipped with a RSA-PE-20 Labsphere[®] integrating sphere. At 0.15% loading, compound (a) imparts to the film a strong UV absorption feature, with a transmittance value less than 10% between 290 and 360 nm and less than 1% between 300 and 340 nm. The photostability of compound (a) is demonstrated by exposing the film sample to UV light in an Atlas Ci 65 Xenon Arc Weather-O-meter[®] (WOM, 63°C black panel temperature, continuous dry cycle, according to ASTM G 26-96). After 1500 hours of WOM exposure the minimum transmittance displayed by the film is still around 1% at 320 nm.

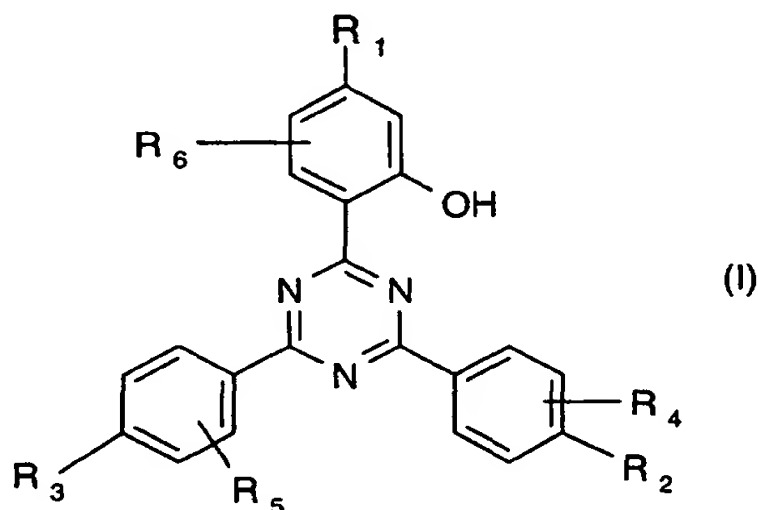
Compound (a) is fully compatible in LDPE film; no blooming is observed after storage of the film for 6000 hours at room temperature. Same behavior is observed keeping the film for the same amount of time in oven at 60°C. After the same time of exposure in oven, no significant change in the UV-Vis absorption spectrum is observed, meaning there is no loss of additive, because of the high temperature.

WOM exposure of the formulation reported in this example is continuing, in order to evaluate the light stability performance of the polymer containing compound (a). Samples are also being exposed to natural weathering and are subjected to treatments with pesticides, in order to evaluate the resistance to chemicals that can be employed in agriculture.

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WHAT IS CLAIMED IS:

1. Transparent polyolefin article stabilized against the effects of light, oxygen, heat and aggressive chemicals by addition of 0.005 - 0.30 % by weight the polyolefin of a hydroxyphenyl triazine UV absorber, characterized in that the article has a thickness between 1 and 500 μm .
2. Transparent polyolefin article of claim 1 containing as further stabilizer a sterically hindered amine.
3. Transparent polyolefin article of claim 2 containing the sterically hindered amine in an amount of 0.01 - 6 % by weight the polyolefin.
4. Transparent polyolefin article of claim 3 wherein the weight ratio sterically hindered amine : hydroxyphenyl triazine UV absorber ranges from 2 : 1 to 20 : 1.
5. Transparent polyolefin article of claim 2 wherein the sterically hindered amine belongs to the class of hydroxylamine ethers.
6. Transparent polyolefin article of claim 1 wherein the hydroxyphenyl triazine UV absorber conforms to the formula I



wherein

R_1 is H or OR_7 ;

R_2 and R_3 independently are H, , OR_9 ;

R_4 and R_5 independently are H, $\text{C}_1\text{-C}_8$ alkyl, OR_{10} ;

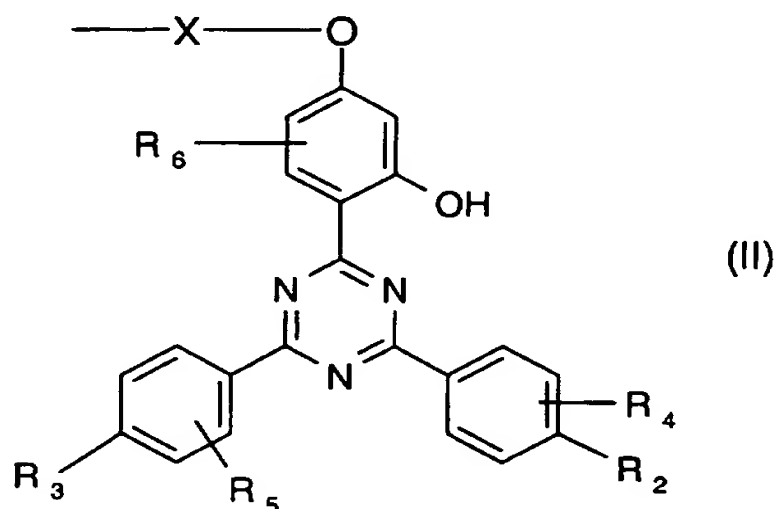
R_6 is H, $\text{C}_1\text{-C}_{18}$ alkyl, $\text{C}_5\text{-C}_{12}$ cycloalkyl, $\text{C}_7\text{-C}_{12}$ phenylalkyl, $\text{C}_7\text{-C}_{12}$ alkylphenyl, $\text{C}_3\text{-C}_{12}$ alkenyl, halogen, OH, OR_9 ;

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R_8 is H; halogen; C_1 - C_{12} alkoxy; C_1 - C_{12} alkyl; C_3 - C_{24} alkyl interrupted by oxygen and/or substituted by OH; or is $NH-CO-R_{14}$ or $NH-COO-R_{12}$;

R_7 , R_9 and R_{10} independently are H; C_1 - C_{24} alkyl; C_3 - C_{12} alkenyl; C_3 - C_{24} alkyl interrupted by oxygen and/or substituted by OH; or is C_5 - C_{12} cycloalkyl, C_7 - C_{12} phenylalkyl, C_7 - C_{12} alkylphenyl; $CH_2CH(OH)CH_2OR_{11}$; C_1 - C_{12} alkyl substituted by $COOR_{12}$, $CONR_{13}R_{14}$, $OCOR_{15}$, OH or halogen;

and R_7 also embraces a residue of formula II



wherein X is C_2 - C_{24} alkylene; $-CH_2CH(OH)CH_2-$; $-CH_2CH(OH)CH_2O-D-OCH_2CH(OH)CH_2-$; $(C_1$ - C_{18} alkylene)- $CO-O-D-O-CO-(C_1$ - C_{18} alkylene); CO ; $CO-(C_2$ - C_{24} alkylene)- CO ; C_3 - C_{24} alkylene interrupted by oxygen;

D is C_2 - C_{12} alkylene; C_4 - C_{50} alkylene interrupted by O; phenylene; biphenylene or phenylene-E-phenylene;

E is O, S, SO_2 ; CH_2 ; CO or $-C(CH_3)_2-$;

R_{11} is H, C_1 - C_{12} alkyl; phenyl; phenyl substituted by 1-3 C_1 - C_4 alkyl; C_5 - C_{12} cycloalkyl; C_7 - C_{12} phenylalkyl; C_3 - C_{12} alkenyl;

R_{12} is H; C_1 - C_{24} alkyl; C_3 - C_{12} alkenyl; C_3 - C_{36} alkyl interrupted by oxygen and/or substituted by OH; or is C_5 - C_{12} cycloalkyl, C_7 - C_{12} phenylalkyl, C_7 - C_{12} alkylphenyl; phenyl;

R_{13} and R_{14} independently are H, C_1 - C_{18} alkyl; phenyl; phenyl substituted by 1-3 C_1 - C_4 alkyl and/or C_1 - C_4 alkoxy; C_5 - C_{12} cycloalkyl; C_3 - C_{12} alkenyl;

R_{15} is C_1 - C_{12} alkyl; phenyl; phenyl substituted by 1-3 C_1 - C_4 alkyl and/or C_1 - C_4 alkoxy; C_5 - C_{12} cycloalkyl; C_3 - C_{12} alkenyl; C_1 - C_{12} alkoxy; or is $NR_{13}R_{14}$.

7. Transparent polyolefin article of claim 6, wherein in formula I

R_4 and R_5 and R_6 independently are H;

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R₈ is H; C₁-C₈alkoxy; C₁-C₈alkyl;

R₇, R₉ independently are H; C₁-C₁₈alkyl; C₃-C₁₂alkenyl; C₃-C₂₄alkyl interrupted by oxygen and/or substituted by OH; or is C₅-C₁₂cycloalkyl, C₇-C₁₂phenylalkyl, C₇-C₁₂alkylphenyl; C₁-C₁₂alkyl substituted by COOR₁₂, OCOR₁₅, OH;

and R₇ also embraces a residue of formula II, wherein X is C₂-C₁₈alkylene; -CH₂CH(OH)CH₂-; -CH₂CH(OH)CH₂O-D-OCH₂CH(OH)CH₂;

(C₁-C₄alkylene)-CO-O-D-O-CO-(C₁-C₄alkylene); CO; CO-(C₂-C₁₈alkylene)-CO;

C₃-C₁₈alkylene interrupted by oxygen; D is C₂-C₁₂alkylene;

R₁₂ is H; C₁-C₂₄alkyl; C₃-C₁₂alkenyl; C₃-C₂₄alkyl interrupted by oxygen and/or substituted by OH; or is C₅-C₁₂cycloalkyl, C₇-C₁₂phenylalkyl, C₇-C₁₂alkylphenyl; phenyl;

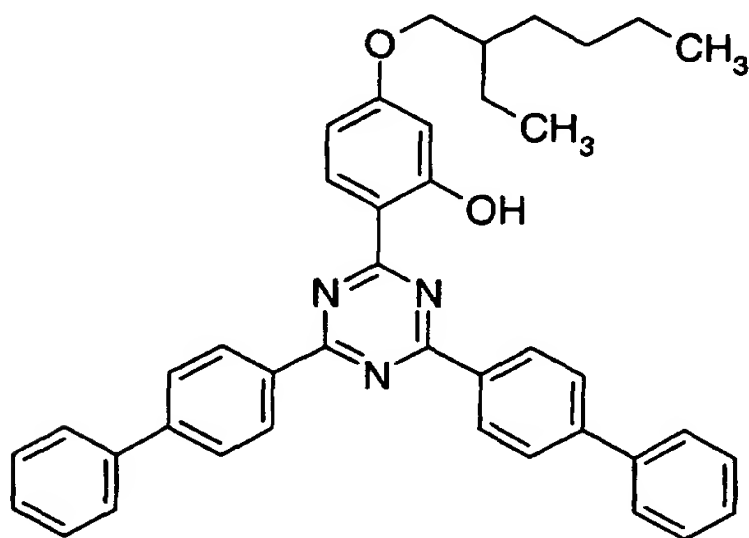
R₁₅ is C₁-C₁₂alkyl; C₅-C₁₂cycloalkyl; C₃-C₁₂alkenyl.

8. Transparent polyolefin article of claim 1 which is a film or layer having a thickness between 1 and 300 μm, especially between 1 and 200 μm.
9. Use of the transparent polyolefin film of claim 8 for suppressing microbial growth in a protected cultivation.
10. Process for suppressing microbial growth in a protected environment, which process comprises covering the environment with the transparent polyolefin film of claim 8.
11. Process of claim 10, wherein the protected environment is a plant cultivation.
12. A method for selectively screening solar and/or artificial light radiation to crops contained inside a green house which comprises covering said green house with the polyolefin film of claim 8.
13. Transparent polyolefin article of claim 1, wherein the polyolefin is polyethylene or polypropylene.
14. Transparent polyolefin article of claim 1 which is a film, fiber, ribbon or stretched tape, especially an agricultural film.

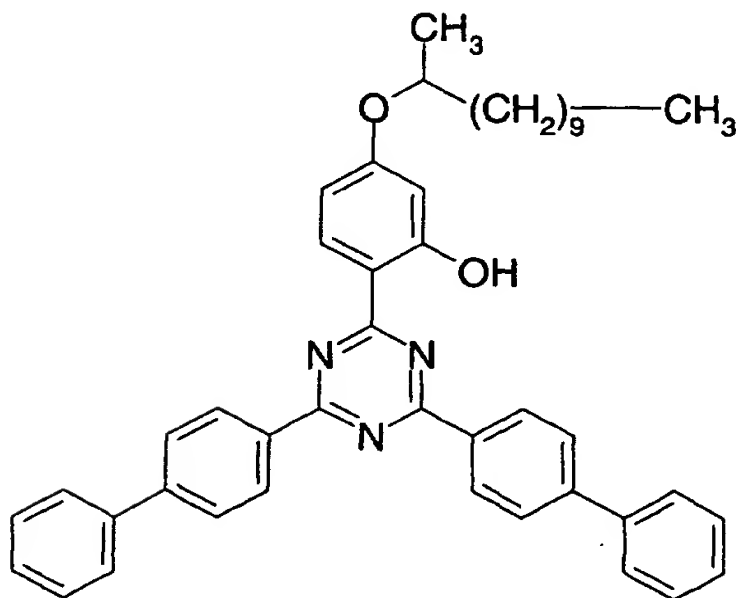
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15. Transparent polyolefin article of claim 1 or 2 additionally containing a further component, especially a further light stabilizer, processing stabilizer, filler, clarifier, modifier or acid scavenger.
16. A compound of one of the formulae a, b, f, g or h

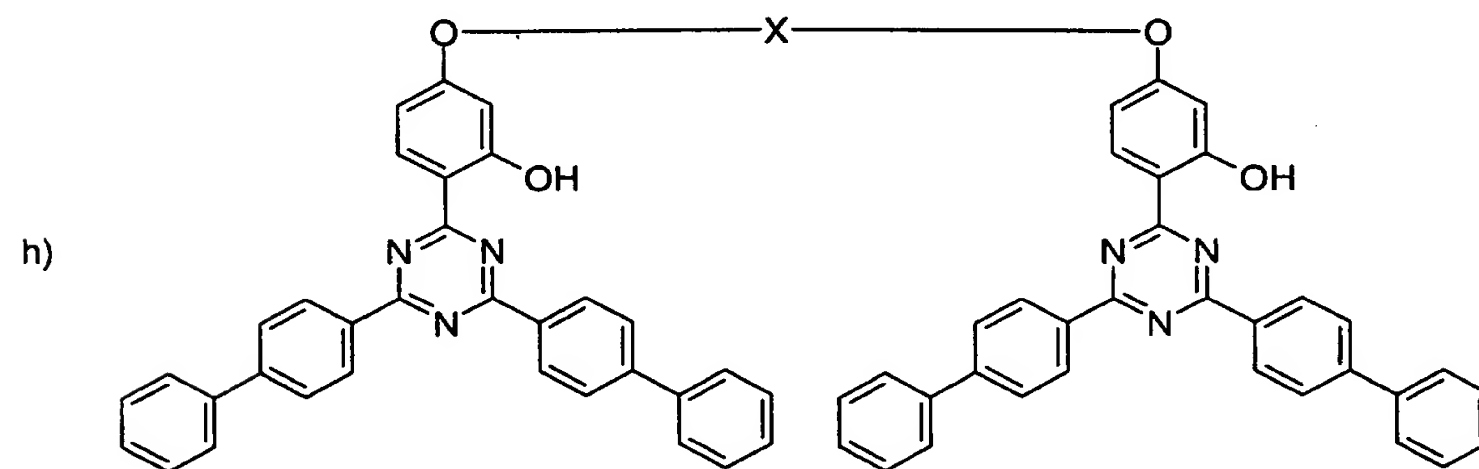
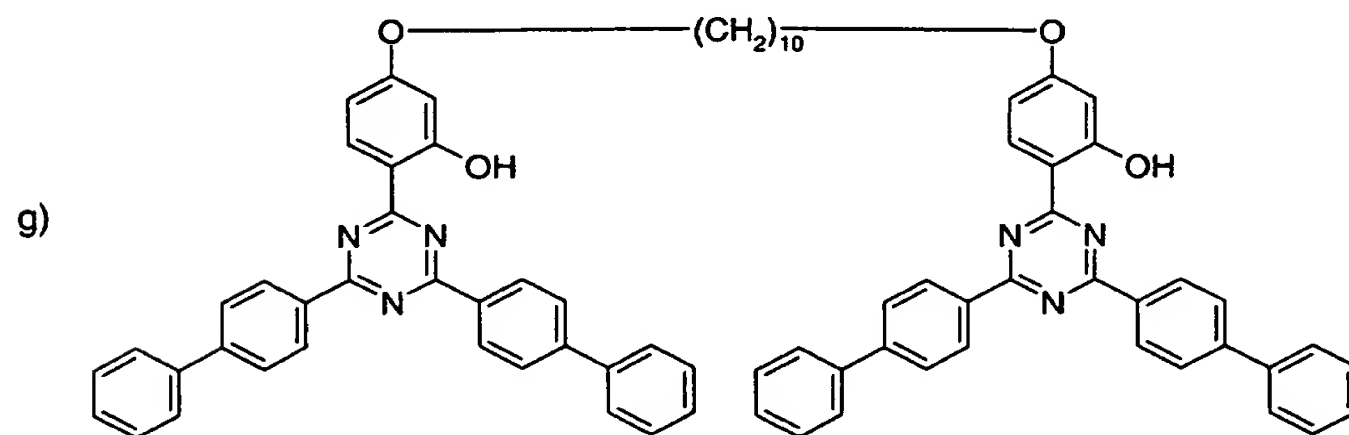
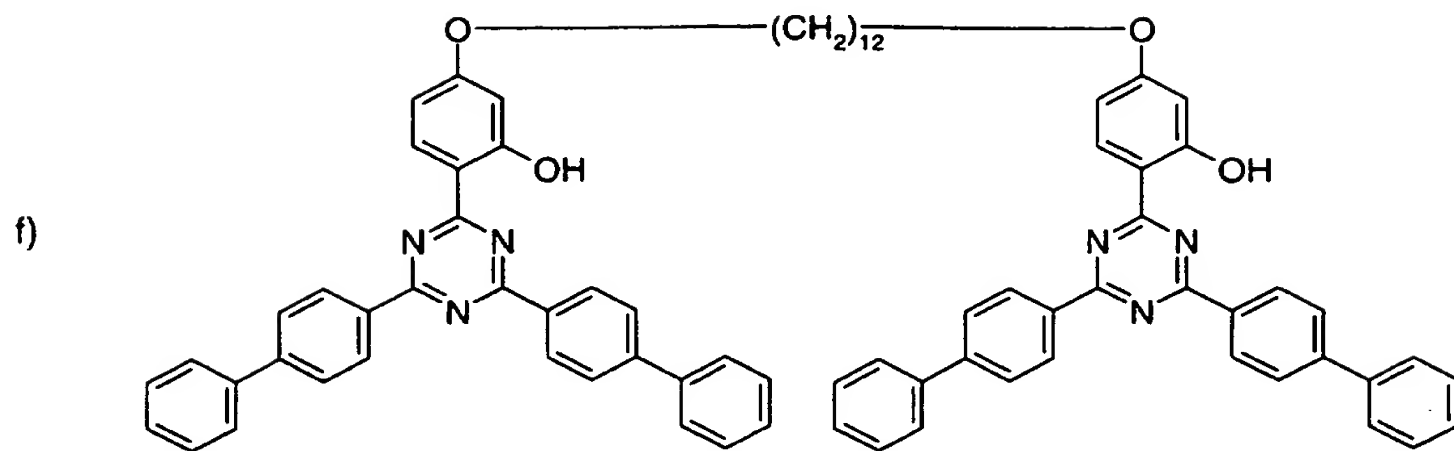
a)



b)



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wherein X is C₁₃-C₂₄alkylene; (C₁-C₁₈alkylene)-CO-O-D-O-CO-(C₁-C₁₈alkylene); CO-(C₁₃-C₂₄alkylene)-CO;

C₃-C₂₄alkylene interrupted by oxygen, especially (C₁-C₃alkylene)-O-(C₁-C₃alkylene).

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Abstract

The novel transparent polyolefin article disclosed is stabilized against the effects of light, oxygen, heat and aggressive chemicals by addition of 0.005 - 0.30 % by weight the polyolefin of a hydroxyphenyl triazine UV absorber, and is characterized by its thickness between 1 and 500 μm . Preferred polyolefin articles thus stabilized are agricultural films containing as further stabilizer a sterically hindered amine. The novel compositions act as selective UV filter especially useful for agriculture.

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